

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Process for the Treatment of Aluminiumsilicates of the kind of Montmorillonite for the Treatment of Beer or Wort

We, DEGLUTAN (BEER PRODUCTS) LIMITED, of 26/27, Conduit Street, London, W.1, a Company organised according to the laws of Great Britain, 5 do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 It is known to treat wort or beer itself with aluminium silicates of the type of montmorillonite in order to improve the properties of the beer especially its resistance towards turbidity caused by coldness 15 or by pasteurisation. Amongst the several aluminium silicates of this type, natural bentonite as it is obtained in America has been found most suitable of all. Furthermore, it has already been proposed to 20 transform aluminium silicates which are not capable of swelling as for example calcium bentonite into a suitable form for the treatment of beer in that they are treated with solutions of alkali metal salts 25 with continuous renewing of the liquid whereby the corresponding concentration of the solution is kept up. The aluminium silicate capable of swelling thus obtained is also very suitable for the above mentioned purpose.

The aluminium silicates known as clays can be divided into two classes, namely, the kaolin clays and the montmorillonite clays, which differ in their chemical 35 structure and particularly in their crystalline lattice structure, as shown by their X-ray spectra. Whereas kaolin and related clays give up practically no water up to 400° C., and then at 450° C. lose 40 practically the whole crystal water, with a rupture of the crystal lattice, the water of swelling in the crystalline lattice of montmorillonite and clays of that type is given up gradually already at low temperatures up to 550° C.

45 Members of the aluminium silicate family of the type of montmorillonite

include not only the pure mineral but also the bentonites and numerous bleaching earths. In so far as these latter have the 50 crystal structure previously indicated, they are included in the scope of this invention.

In some cases the content of arsenic causes difficulties in the case of natural 55 bentonite which is capable of swelling as well as in the case of aluminium silicates treated in the above mentioned manner. The arsenic content is indeed only of the order of a few milligrams per kilogram of 60 aluminium silicate so that damage to health need not be feared. In some countries, as, for example, Great Britain, the health laws are so strict that these 65 aluminium silicates for the stabilisation of beer may not be imported if their arsenic content exceeds a certain limit.

The known processes which are used for the working up and analysis of arsenic-containing minerals cannot be applied to 70 the treatment of bentonite or other aluminium silicates of similar structure without modification, especially if the minerals are to be obtained in a form which appears suitable for the treatment 75 of wort or beer. The problem thus arose to work out a suitable process to remove the arsenic completely or at least extensively from these minerals so that no further objections could be raised against 80 their use for the treatment of wort or beer even under the very strictest requirements and the product is nevertheless obtained in a suitable form for the treatment of 85 drinks.

According to the present invention this task can be solved very readily, and in a surprising manner, in that the arsenic-containing aluminium silicate of the type of montmorillonite as hereinbefore defined 90 is treated with hydrochloric acid which dissolves the arsenic and which is then separated from the aluminium silicate. The concentration of the hydrochloric

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acid must be at least 5% and lies preferentially between 10 and 15%. The duration of the treatment is dependent upon the nature of the aluminium silicate, on its arsenic content, and on the working temperature. In general it requires one or several hours up to one or several days. The treatment itself is either carried out with a single application when the hydrochloric acid is decanted from time to time or in a continuous process when the raw material is stacked in a vessel and the acid is allowed to flow through it slowly, being preferably added from above while the spent acid is withdrawn from below by a siphoning arrangement.

The extraction with hydrochloric acid is followed by a process of washing out, preferably in the same apparatus, with a solution of a neutral salt of an alkali metal such as sodium chloride of such a concentration that swelling is inhibited. In this manner the lattice structure of the aluminium silicate is maintained and its typical swelling properties are preserved.

#### EXAMPLE.

The process was carried out in an apparatus which consisted of two earthenware vessels of 100 and 400 litres capacity. A solution of hydrochloric acid and later a solution of common salt was put into the smaller vessel wherefrom the solution was allowed to flow into the bigger vessel which contained the aluminium silicate to be treated. A layer of broken glass bottles and porcelain balls was stacked on the bottom of the treatment vessel in order to avoid the material being carried away by the liquid with consequent losses and stoppages. The aluminium silicate was deposited upon this layer. In order to determine the effectiveness of the treatment two experiments were carried out.

1. 50 kg of bentonite containing 6.1 mg As/kg were mixed in a coarse-grained condition with 65 litres of a 10% solution of hydrochloric acid so that the crude material was covered by liquid. After the hydrochloric acid had acted for 24 hours it was drawn off which required about 3 hours. The acid was then washed out by treating the material with 300 litres of a 10% solution of common salt in a continuous process which required 8 to 10 hours. A little ammonia was added to the solution of common salt to help the neutralisation process.

The washing was continued until the filtrate reacted neutral towards litmus.

60 The treated material contained 1.2 mg As/kg.

2. Although this arsenic content was already below the allowed maximum limit of 1.4 mg As/kg according to the British

law, the aluminium silicate treated in the above mentioned method was yet again subjected to a similar treatment. Only 50 litres of a 10% solution of hydrochloric acid were necessary for this purpose as the aluminium silicate was already moist. The time of action of the hydrochloric acid upon the substance was again 24 hours. 300 litres of a 10% solution of common salt were then again used for washing out.

75 After this second treatment the material showed a content of 0.8 mg As/kg.

80 The determination of the arsenic content is carried out according to the Gutzeit method modified by Sanger and Black as described in Proc. amer. Acad. Act. U. Sc. No. 8, 1907 and Zeitschrift anorg. Chemie 58, 1908. This example shows that by the treatment with hydrochloric acid the arsenic content can be reduced unobjectionably and in the required quantity. Other experiments have shown that the concentration of the hydrochloric acid can be reduced down to 5%. As the loss in weight which takes place in the treatment with acid is only 2%, this signifies that the process is quite an economic one. The adsorption capacity of the bentonite towards the albumen removed from the wort or the beer was determined by the Eshbach reaction. It was shown that it is reduced by only a small amount by the treatment with acid. This small decrease in efficiency can be balanced by making a small increase in the amount of silicate added.

90 If the starting material is calcium bentonite which is incapable of swelling, for example, that of European origin, the process for the removal of arsenic can then be combined with the transformation into a material capable of swelling. The calcium bentonite is in this case first treated in a crude form with hydrochloric acid. After the arsenic content has been reduced to the required value the material is then treated with a solution of common salt in the same vessel until the capability for swelling has been achieved. The replacement of the calcium ion by the sodium ion thus also occurs simultaneously with the neutralisation of the product.

105 The salts contained in the finished product occur in such small quantities that by the use of the material for the treatment for wort or beer no taste or other influence can be noticed.

110 If the continuous process is used then one litre of hydrochloric acid is on the average sufficient for the treatment of one kg of aluminium silicate. It is thereby possible to recycle the used acid and to use it several times.

If on the other hand the treatment is carried out with static hydrochloric acid which is changed from time to time then the amount quoted above should be

5 increased. The solution of common salt used for washing out and regeneration has for this purpose a content of approximately 10% of sodium chloride in order to avoid swelling.

10 In place of the earthenware vessels described in the example other vessels made of acid resisting materials as for example wood, acid resisting steel, etc. or vessels with an acid resisting coating can be 15 used.

The material treated according to the invention can be used not only for the treatment of wort or beer but also for the stabilisation of other liquids as for 20 example wine, edible oils, etc., in other words it can thus be used everywhere where arsenic free properties are stressed.

It should also be mentioned that it is already known to treat fuller's earth and 25 such like with acid in order to activate it. This treatment by acid is however carried out in quite a different way. Above all the treatment by acid is not continued until the arsenic content has decreased below a 30 certain value but only a single treatment by acid of short duration is applied. Furthermore no neutralisation is carried out with fuller's earths activated by acid treatment as the hydrogen ion concentration 35 is then the important factor for the activity.

What we claim is:—

1. A process for the treatment of 40 aluminium silicates belonging to the montmorillonite group as hereinbefore defined for the purpose of removing arsenic characterised in that the aluminium silicate is extracted with hydrochloric acid of at least 5% concentration and that the extracted aluminium

silicate is washed out with a solution of a neutral salt of an alkali metal of such a concentration that swelling is inhibited.

2. Process according to Claim 1 characterised in that the treatment with hydrochloric acid is continued until the arsenic content has fallen below the value of 1.4 milligrams per kilogram. 50

3. Process according to Claim 2 in which the neutral salt used is sodium chloride. 55

4. Process according to any of Claims 1, 2 or 3 characterised in that a small amount of alkali or ammonia is added to the washing out liquid. 60

5. Process according to any of Claims 1 to 4 characterised in that the aluminium silicate in coarse grains of the type of montmorillonite which is not capable of swelling for example calcium bentonite is freed wholly or in part of arsenic and then the bonded polyvalent cations capable of being exchanged are replaced by monovalent cations by treatment with solutions of alkali metal salts with constant renewing of the solution. 65

6. A process according to Claim 5 in which the alkali metal used is sodium chloride. 70

7. Process for the treatment of 75 aluminium silicates such as montmorillonite for the purpose of removing arsenic substantially as herein described.

8. Aluminium silicates such a montmorillonite which have been treated by 80 any of the processes claimed in Claims 1 to 7.

9. A process for the treatment of beer or wort by treating it with the silicates claimed in Claim 8. 85

10. Beer or wort which has been treated by the process claimed in Claim 9.

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